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16. ABSTRACT

Using research results reported from oil spills, laboratory experiments and microcosm studies, this review outlines the many processes controlling the behavior of petroleum in marine waters. The fate of oil spilled at sea depends on the composition of the oil, and on such external factors as light and temperature. The extent of degradation depends on the type of coastal areas in which the spill occurs. In open, exposed areas, with good circulation of water, most oils are quickly degraded (Rashid, 1974). In protected shallow areas with poor-circulation spilled oil is incorporated into the fine sediment and much remains unaltered for many years (Blumer and Sass, 1972). Photochemical oxidation, dissolution, emulsification, adsorption to particles, biodegradation and uptake by zooplankton interact to affect the fate of oil slicks and oil in the water. Sedimentation deposits oil on the bottom where it can be resuspended into the water, penetrate deeper into the sediment or be degraded. The sediment community of microbes, meiofauna and macrofauna is responsible for the degradation of sediment oil.

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CHAPTER 12

PROCESSES AFFECTING THE FATE OF OIL IN THE SEA

Richard F. Lee

INTRODUCTION

Each year millions of tons of oil enter the ocean. Sources include marine transportation, offshore oil production, coastal oil refineries, sewage outfalls, natural seeps and atmospheric fallout. Various reports have attempted to determine the relative importance of these various inputs (O.A.B., 1975; Van Vleet and Quinn, 1978). On a worldwide basis the largest contributors are oil-production and -transport operations. In some harbors and bays in the U.S.A. sewage outfalls can be the major source of oil pollution.

A variety of physical, chemical and biological processes affect the fate of spilled oil (Fig. 1). Physical and chemical processes rapidly act on oil slicks which generally results in their disappearance within a few days. Components of oil which enter the water also have a short residence time with some being carried to the bottom by sedimentation. The bottom sediments are the ultimate sinks for undegraded oil. For discussion purposes this chapter has separate sections on processes acting on oil slicks, oil in water and oil in sediments.

FATE OF OIL IN SLICKS

Following discharge of oil into water a slick forms due to the low water solubility of most oil components. Currents, waves and winds act to spread the oil slick into thin films. Fallah and Stark (1976) reviewed theories and models which describe the movement of oil on water. The models develop empirical equations which take into account the volume of oil spilled and its physical properties, elapsed time and wind speed. For example, heavy viscous oils do not spread as rapidly as less viscous types. In the open sea, wind often determines the direction and speed with which a slick moves with oil drift velocity about 3% of the wind velocity. In nearshore areas tidal forces can control the movement of oil. Determination of slick-transport and -spreading data for a particular area is best done by carrying out experimental field spills. P. G. Jeffrey (1973) followed an experimental spill of 120 t of light Iranian crude oil in the North Atlantic. The slick was followed for four days after which time it rapidly disappeared.

Processes responsible for the disappearance of a slick include evaporation,

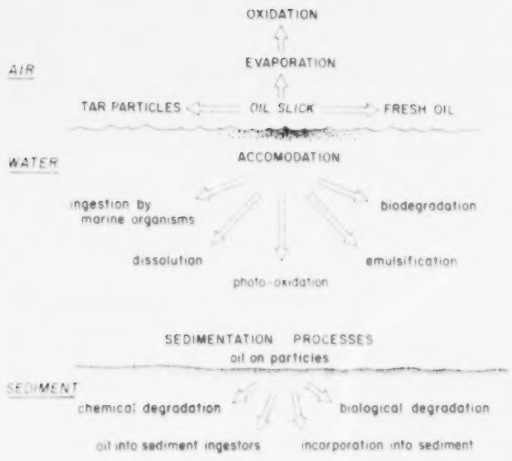

Fig. 1. Fate of oil at sea.

dissolution, emulsification, photochemical oxidation and microbial degradation. A first-order equation describes the oil concentration changes resulting from these processes:

$$dc/dt = (K_V, K_E, K_D, K_P, K_B)C$$

K_V, K_D, K_P, K_E, K_B are evaporation, dissolution, photochemical, emulsification and biological decay coefficients, respectively. The approximate decay coefficients for evaporation and dissolution, the primary forces removing slick components during the first few days, have been determined by W. P. James (cited in Harrison, 1974) for different oil fractions. The time required and the relative importance for the various oil weathering processes are summarized (Fig. 2).

Evaporation acts to remove volatile components as soon as a slick forms. Hydrocarbons below C_{15} (boiling point $< 270°$ C) volatilize in a few days (Harrison et al., 1975; O.A.B., 1975; McAuliffe, 1977a). This volatile fraction comprises 20—50% of most crude oils and 75% or more of many fuel oils. Hydrocarbons in the C_{15}—C_{25} range (boiling point = 250°—400° C) are volatilized from an oil slick only to a limited extent. The rate of evaporation is affected by temperature, wind speed, solar radiation, thickness of the slick and composition of the oil. In an experimental 1.04-m^3 (275-gal.) experimental crude oil spill in the Bahamas all low-weight aromatics disappeared with the first 90 min. (Harrison, 1974). The water temperature was 24° C and wind speed ranged from calm to 30 km $hr.^{-1}$. It was estimated that one third of the oil from the "Torrey Canyon" spill evaporated (Brunnock et al., 1968)

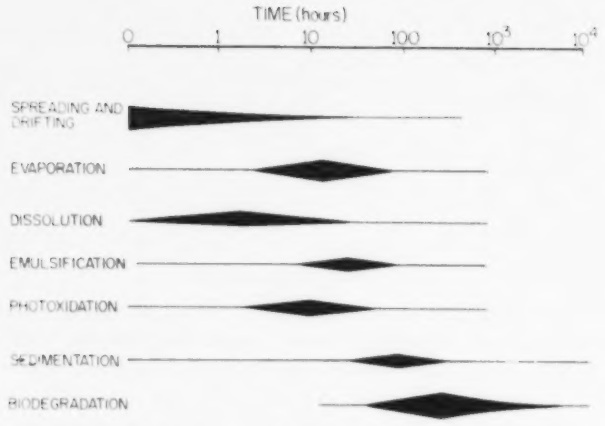

Fig. 2. Relative importance of various processes affecting oil.
Modification of a figure from Koons and Wheeler (1977). *Line length* is the probable time span of a process. *Line width* is the relative magnitude of the process.

Dissolution is the dispersal of oil into water. This includes dissolved compounds and small dispersed oil droplets. Following a spill of a heavy fuel oil in Chedabucto Bay, Nova Scotia, small particles of oil (0.01—1 mm in diameter) were in the upper water along the Nova Scotia coast (Forrester, 1971). It was estimated that 107 of 9500 t spilled went into particles. This heavy fuel oil had a density of $0.97\,g\,ml^{-1}$. Lighter fuel oils do not form droplets or particles of oil which remain in the water. The solubility of hydrocarbons drops exponentially as a function of their molecular volume so that low-weight aromatics have relatively high solubility (McAuliffe, 1966). Toluene, naphthalene, phenanthrene and chrysene are an aromatic series with an increasing number of rings and their solubilities in water are 515, 32, 1 and $0.002\,mg\,l^{-1}$, respectively (Mackay and Shiu, 1977). Thus, under oils slicks the predominant components are low-weight aromatics, such as a benzene, toluene and xylenes. Under an experimental oil spill off the U.S.A. east coast the concentration of aromatics at a depth of 1.5 m was $50\,\mu g\,l^{-1}$ (McAuliffe, 1977b). Studies after a large crude oil spill in the Gulf of Mexico showed less than 1% of the oil was in the water (McAuliffe et al., 1975). In an experimental crude oil spill carried out in a tank 5% of the spilled oil entered the water (Gordon et al., 1976).

Evaporation and dissolution are simultaneous and competitive processes. Each hydrocarbon evaporates and goes into solution at rates depending upon its vapor pressure and water solubility (McAuliffe, 1977a). In most areas evaporation is far more important in removing oil slick components than is dissolution. Based on evaporation rate equations, Harrison et al. (1975) predicted that evaporation of aromatic hydrocarbons would be 100 times faster

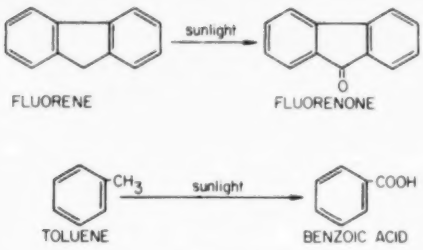

Fig. 3. Oxidation products produced during the photo-oxidation of oils.

than solution of these compounds. However, in areas of low temperature and high turbulence, such as polar seas, dissolution may result in relatively high concentrations of low-weight aromatics under a spill. Turbulence increases the surface/volume ratio of the spilled oil and thus enhances dissolution. Dissolution of an oil slick can also be promoted by naturally occurring surfactant, such as humic acids and fatty acids, which tend to be concentrated in the surface microlayer (Boehm and Quinn, 1974). Solar radiation can photochemically degrade certain oil components to polar, surface-active molecules which promote the dissolution of the oil.

Surface-active components in crude oil, such as porphyrins and carboxylic acids, help to form water-in-oil emulsions, sometimes referred as "chocolate mousse" (Canevari, 1969) because of its color and consistency. This stable emulsion floats on the water and eventually can be carried ashore by wind and waves. Strong turbulent mixing can drive emulsified oil into the water column. Fuel oil or other refined petroleum products with no surfactants do not form water-in-oil emulsions. The time required for the formation of water-in-oil emulsions varies from a few hours to several days depending on the nature of the oil (O.A.B., 1975).

The processes discussed above distribute the components of oil slicks into different phases, i.e. air or water, but do not degrade the compounds. Photo-oxidation and microbial degradation are the primary processes responsible for degrading the compounds in oil slicks. Energy from sunlight in the presence of oxygen can transform hydrocarbons into a number of oxygenated compounds. Because of their relatively high water solubility, the products of photo-oxidation, including carboxylic acids, alcohols, ketones and phenols, are detected in the water below oil slicks which have been exposed to ultraviolet irradiation (Hansen, 1975, 1977; Larson et al., 1976). The aromatic hydrocarbons in oil are degraded by light more rapidly than aliphatics, and branched-chain aliphatics are degraded more rapidly than straight-chain aliphatics. Photo-oxidation products which have been isolated include fluorenone and benzoic acid (Hansen, 1975; Larson et al., 1976; Fig. 3). The ultraviolet and near-ultraviolet areas of the spectrum are responsible for degradation since exposure to light above 350 nm does not result in oil degradation (Hansen, 1977). Hansen (1975) calculated that a 0.04-mm film

of fuel oil would require three years to photochemically degrade. However, very thin oil films can be photochemically degraded in a few days (Freegarde and Hatchett, 1970).

Because of the time needed for initiation of microbial degradation of oil slicks, which have short lifetimes, it is assumed that microbial degradation is less important than other processes above-discussed in slick removal. Once the oil is dispersed into fine droplets or particles in the water or deposited on sediment, microbial degradation becomes of great importance.

After evaporation, dissolution, emulsion, photo-oxidation and biodegradation have acted on an oil slick to remove the lighter-weight components what remains is a more viscous residue. This residue or tar balls contain higher-weight hydrocarbons and oxygen- and sulfur-containing compounds, sometimes referred to as asphaltenes. The percentage of crude oil which remains as a residue varies for different oils. Butler et al. (1976) suggested that as much as 20% of a crude oil will remain as a residue. The presence of tar balls in the Mediteranean and North Atlantic has been well documented (Horn et al., 1970; Butler et al., 1973; Levy, 1977). These tar balls are resistant to microbial degradation (S. J. Davis and Gibbs, 1975), and it has been estimated that their lifetime is on the order of several months to a year (Butler et al., 1976).

FATE OF OIL IN WATER

Oil can enter the water phase by dissolution or related processes. The concentration of oil components, whether dissolved or in particles, decreases exponentially due to evaporation, adsorption to suspended particles, sedimentation, photochemical oxidation, uptake by zooplankton or biodegradation (Lee et al., 1978; Gearing et al., 1979). The decrease in the water concentration of some polycyclic aromatics in a dispersions of crude oil added to a marine controlled ecosystem is illustrated in Fig. 4.

Higher-weight aromatics and aliphatics in water adsorb to suspended particles because of their low water solubility while lower-weight hydrocarbons and more polar oil components remained dissolved in the water (Meyers and Quinn, 1973; Herbes, 1977; Lee, 1977; Table I). Sedimentation of particles carries hydrocarbons to the bottom. Studies in estuarine areas have indicated that most dissolved hydrocarbons adsorb to detrital particles, which are mixtures of organic matter, living bacteria and small clay particles (Lee, 1977). Scanning electron micrographs reveal rough surfaces on these detrital particles, with bacteria fastened by mucoid-like pads and fibrillar appendages (Fig. 5). Presumably these surfaces provide hydrophobic areas for hydrocarbon adsorption.

Oil slick and dispersed oil globules adsorb to clays and fine-suspended sediments in seawater and eventually these sediments, with attached oil

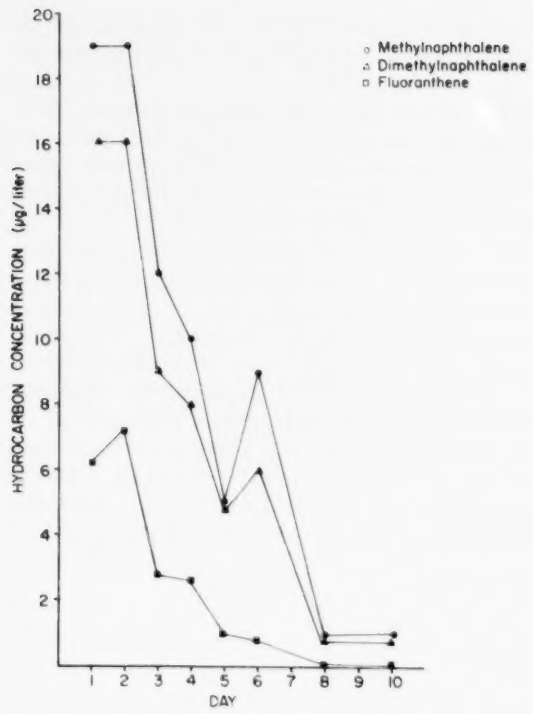

Fig. 4. Concentration changes of polycyclic aromatic hydrocarbons in water after addition of a dispersion of crude oil to a controlled ecosystem.
A dispersion of crude oil enriched with some selected polycyclic aromatic hydrocarbons was added to a controlled ecosystem enclosure (ca. 2 m diameter and 15 m deep $= 6 \cdot 10^4$ l). Water from 3 m was taken at various time intervals, extracted and analyzed for polycyclic aromatic hydrocarbons by high-pressure liquid chromatography. A complete description of the experiment is given in Lee et al. (1978).

globules or oil films, are carried to the bottom (Poirier and Thiel, 1941; Bassin and Ichiye, 1977). In open-ocean areas concentrations of suspended solids are relatively low, rarely exceeding $1\ mg\,l^{-1}$ (Schubel, 1974). In estuaries and other coastal areas the concentration of suspended solids can be quite high. For example, the estuaries of coastal Georgia have an average suspended solid concentration of $50\ mg\,l^{-1}$ with concentrations as high as $600\ mg\,l^{-1}$ during spring tides (Oertel, 1976). After a hurricane the concentration of suspended solids entering one part of Chesapeake Bay rose to $10^4\ mg\,l^{-1}$. In these turbid areas dispersed oil is soon removed by sedimentation. A practical application to accelerate sedimentation was the use of powdered chalk to sink Kuwait crude oil spilled by the "Torrey Canyon" (J. E. Smith, 1968).

TABLE I

Adsorption of hydrocarbons to particles in estuarine waters

Hydrocarbon	Concentration of hydrocarbon in water ($\mu g\, l^{-1}$)	Amount adsorbed to suspended particles (%)
Naphthalene	30	0.7
Methylnaphthalene	30	6
Fluorene	15	12
Benz(a)anthracene	10	53
Benzo(a)pyrene	3	71
Hexadecane	3	8
	10	19
Octadecane	5	22
Anthracene	4	6
	15	22

Radiolabeled hydrocarbons were added to 100 ml of water collected in the Skidaway River, Georgia. The concentration of suspended solids in this estuarine river was 40 $mg\, l^{-1}$. After three hours the water was filtered and the amount of hydrocarbons on particles was determined.

Zooplankton, including copepods and protozoans, can consume particles of oil which are subsequently excreted, unmodified, in the feces (Conover, 1971; A. R. Andrews and Floodgate, 1974). In one oil spill up to 20% of the particulate oil in the water was sedimented to the bottom in zooplankton feces (Conover, 1971). Copepods also take up dissolved hydrocarbons from the water. The copepods posses enzyme systems which metabolize the hydrocarbons to various hydroxylated metabolites which are later excreted (Lee, 1975; Corner et al., 1976).

Bacteria, yeasts and filamentous fungi capable of degrading oil have been isolated from polluted and pristine water (Midget et al., 1969; Ahearn and Meyers, 1972; Floodgate, 1972; Gunkel, 1973; Perry and Cerniglia, 1973). Although occurring in all marine areas, hydrocarbon-degrading microbes are generally more abundant in chronically polluted water (Atlas and Bartha, 1973; Tagger et al., 1976). In the North Sea, oil-degrading bacteria were most abundant near active oil fields (Oppenheimer et al., 1977). The rates of microbial degradation are influenced by temperature and nutrients. Atlas and Bartha (1973) found that the number of oil-degrading microbes was very low during the winter in Raritan Bay, New Jersey. C. F. Gibbs et al. (1975), using a continuous growth chamber with Irish Sea water and Kuwait crude oil, calculated that the microbial oil degradation rate was 30 and 11 $mg\, l^{-1}\, yr.^{-1}$ in the summer and winter, respectively.

Various metabolic pathways used by microbes in degrading aromatic and aliphatic hydrocarbons has been determined by a number of workers

Fig. 5. Scanning electron micrograph of detrital particle from Skidaway [illegible]er, Georgia, showing attached bacteria (19,000×).

(Gibson, 1968; Walker and Cooney, 1973; Kennedy et al., 1975). Aromatic hydrocarbons undergo enzymatic hydroxylation to diols with subsequent ring fission to give a variety of acids and aldehydes (Fig. 6). Alkanes are oxidized to alcohols and then to fatty acids. Since the hydrocarbons are used as source of carbon for growth the final product is carbon dioxide.

A series of tanks containing water and sediments from Narragansett Bay, Rhode Island, have been used to study microbial degradation of polycyclic aromatic hydrocarbons. Some of the tanks served as controls while dispersions of fuel oil were added continually over several months to other tanks

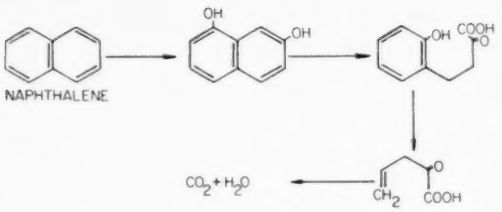

Fig. 6. Metabolic pathway used for the degradation of naphthalene by bacteria. Based on a figure in Gibson (1976).

(Gearing et al., 1979). To measure microbial degradation rates, radiolabeled hydrocarbons were added to water samples followed by collection of $^{14}CO_2$ released. An initial lag before degradation began was observed in water from control tanks (Fig. 7) and the degradation curves resembled the typical log growth curve for bacteria (Pelczar and Reid, 1965). This suggests that initially there were few hydrocarbons-degrading microbes in the water and growth of these microbes began after addition of the hydrocarbon. Studies on the growth of petroleum-degrading bacteria isolated from sediments or water show typical log growth curves (Jobson et al., 1972; Mulkins-Phillips and Stewart, 1974). After addition of fuel oil to the tanks the rates of hydrocarbon degradation increased dramatically and linear degradation curves were observed (Fig. 8). Presumably, the addition of fuel oil causes an increase in petroleum-degrading microbes so there was no lag in degradation after radiolabeled hydrocarbons were added. Degradation rates for naphthalene and methylnaphthalene in the fuel oil treated tank were 1.4 and 1.9 $mg\,l^{-1}\,yr.^{-1}$, respectively (Lee, 1978). This can be compared with crude oil degradation rates of 30 $mg\,l^{-1}\,yr.^{-1}$ in Irish Sea water (C. F. Gibbs et al., 1975).

Photo-oxidation, in addition to acting on oil slicks, as above-discussed, can also degrade components of oil in the water. Ultraviolet light does not penetrate into water and many of the short wavelengths present in the visible region attenuate a few meters below the surface. Some high-molecular-weight polycyclic aromatic hydrocarbons are degraded by light longer than 300 nm, e.g. benzo(a)pyrene, and can be completely photo-oxidized in seawater within a few days after exposure to sunlight (Andelman and Suess, 1970).

All of the processes discussed above act simultaneously to modify the oil. An example of photochemical oxidation combined with microbial degradation is illustrated in Fig. 9. Radiolabeled dimethylbenz(a)anthracene was not microbially degraded in estuarine water in the dark. However, when the water with dimethylbenz(a)anthracene was exposed to sunlight rapid degradation to $^{14}CO_2$ occurred. Presumably, photo-oxidation products of dimethylbenz(a)anthracene were further degraded to CO_2 by microbes.

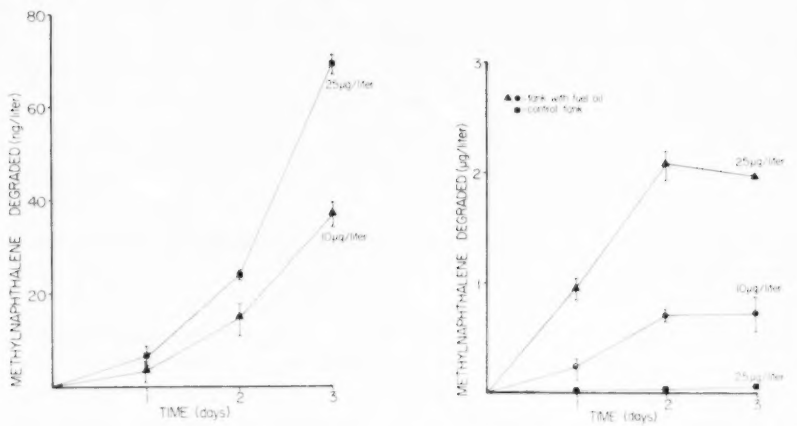

Fig. 7. Amount of ^{14}C-methylnaphthalene degraded with time in water from Narragansett Bay, Rhode Island.
Water taken from a tank containing Narragansett Bay water. ^{14}C-methylnaphthalene (3.7 mCi mM^{-1}) was added to water taken from the tank to give a concentration of 10 and 25 μg l^{-1}. The amount of degradation was determined by collecting $^{14}CO_2$ produced after 1, 2 and 3 days. Temperature was 7° C.

Fig. 8. Amount of ^{14}C-methylnaphthalene degraded with time in water from fuel oil and control tanks.
Dispersions of fuel oil were added to one tank containing Narragansett Bay, Rhode Island, water and sediment over a 3-month period, while a second tank served as a control. ^{14}C-methylnaphthalene (3.7 mCi mM^{-1}) was added to water from control or fuel oil treated tanks to give a concentration of 25 μg l^{-1}. The amount of degradation was determined by collecting $^{14}CO_2$ produced at the different time intervals. Temperature was 23° C. A complete description of the procedures used are given in Gearing et al. (1979).

FATE OF OIL IN SEDIMENTS

Although difficult to quantify in the field, sedimentation processes carry significant amounts of oil to the bottom. The large quantities of oil on the bottom after a drilling platform spill in the Santa Barbara Channel, California, was believed to be due to adsorption of oil to suspended sediments derived from river runoff (Kolpack, 1971). In shallow areas masses of oil can be rolled along the bottom by waves and currents eventually washing ashore to form hard, tarry masses (Clark and Macleod, 1977). Also floating tar balls or emulsions of oils can be washed ashore by these same forces. Stranded oil undergoes various weathering processes but the high-boiling components in the larges masses of oil persist for many years (Blumer et al., 1973). The sinking of the supertanker "Amoco Cadiz" off France resulted in the release of $21.6 \cdot 10^4$ t of crude oil (Hess, 1978). Approximately $6 \cdot 10^4$ t of this oil came ashore during the first two weeks after the spill.

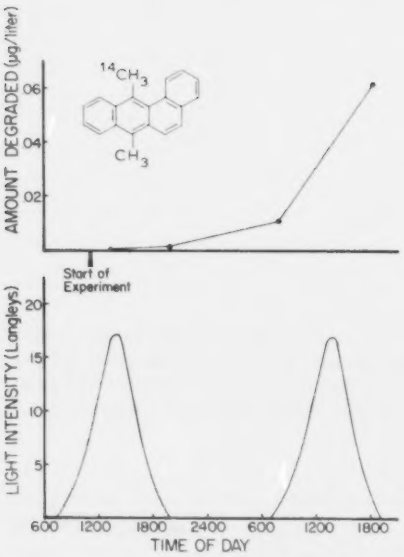

Fig. 9. Photochemical and microbial degradation of *7,12*-dimethylbenz(a)anthracene. *7,12*-dimethyl(*12*-^{14}C)benz(a)anthracene was added to an estuarine water sample (Skidaway River, Georgia) to give a final concentration of 10 $\mu g\, l^{-1}$. Amount of degradation was determined by collecting $^{14}CO_2$ produced at the different time intervals. The water (100 ml) was in a quartz flask suspended in the river which allowed penetration of wavelengths longer than 200 nm. No $^{14}CO_2$ was produced when the experiment was conducted in the dark.

In addition to lateral movement on the bottom oil can penetrate deeper into the sediment, be resuspended into the overlying water or be degraded. Radiolabeled benz(a)anthracene, a four-ringed aromatic hydrocarbon, was dissolved in a fuel oil dispersion which was added to a tank containing Narragansett Bay water and sediments. The concentration of the compound decreased exponentially in the water column and after 10 days approximately 80% had reached the sediment. The penetration of benz(a)anthracene into the sediment is shown in Fig. 10. On day 10 most of the sediment benz(a)anthracene was in the top 1 cm. Cores from days 60, 86 and 126 showed the compound distributed down to 3 cm. Below 3 cm most of the radioactivity was in the form of metabolites, possibly in the interstitial water. Penetration into the sediment was believed due to various mixing processes, including bioturbation. Ten months after a fuel oil spill in Buzzards Bay, Massachusetts, cores showed oil had penetrated to 7 cm (Blumer and Sass, 1972). Turbulent mixing as a result of waves and other forces are probably responsible for the deeper penetration of oil in shallow waters.

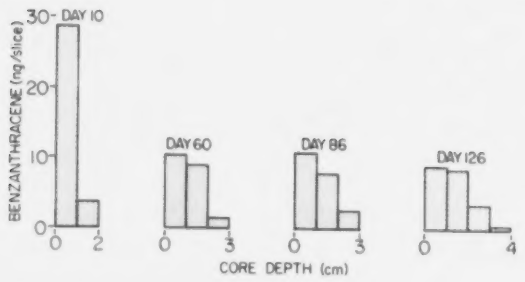

Fig. 10. Penetration of benz(a)anthracene into sediment.
Radiolabeled benz(a)anthracene was dissolved in a fuel oil dispersion which was added to a tank containing 30,000 l of Narragansett Bay, Rhode Island, water and a 30-cm layer of sediment. Cores (area of 1.77 cm^2) were taken at the indicated time intervals and slices made at 1-cm intervals. Each slice was extracted and benz(a)anthracene counted after separation by thin-layer chromatography.

Tidal flow causes resuspension of fine sediments with their associated hydrocarbons. These resuspended sediments can be ingested by benthic filter feeders, such as clams, mussels and oysters. Oil in the feces of these animals can release oil into the water. J. D. Smith and Hopkins (1972) found storm-generated transport of bottom sediments on the U.S.A. continental shelf in water as deep as 80 m. The strong forces generated by hurricanes can mix the top 10 cm of surface sediments in water as deep as 35 m (Hayes, 1967). Thus, Hoffman and Quinn (1978) suggested that mobility of sediment was a factor in the low concentration of oil in the bottom sediments after the "Argo Merchant" spill in the North Atlantic.

In some coastal areas oil-derived hydrocarbons remain in the sediments for many years after a spill (Blumer and Sass, 1972; Scarrutt and Zitko, 1972; Vandermeulen and Gordon, 1976). Coarser bottoms, i.e. composed of sand or gravel, allows greater penetration than fine unconsolidated sediments (Gundlach and Hayes, 1978). The highest concentrations of oil are generally associated with silt-sized sediments possibly because these sediments have a greater area for adsorption of oil (Meyers and Quinn, 1973; Hargrave and Phillips, 1975) (see also Chapter 9 in Volume 2 by Eisma).

Coarser sediments, although allowing greater oil penetration, also have high biodegradation rates relative to fine sediments, possibly because of greater aeration and nutrient flow to the subsurface. Also coarser sediments are associated with more exposed coasts so that all of the weathering forces are effective.

The main factor affecting the persistence of oil in sediments is the rate of biodegradation. Most rapid degradation occurs on the surface, i.e. at the water–sediment interface (Hughes and McKenzie, 1975; Lee, 1978; W. S. Gardner et al., 1979; Lee et al., 1979). Microbial activity is low below the

surface and oil a few centimeters down can remain unmodified for years (Hughes and McKenzie, 1975; W. S. Gardner et al., 1979). In many estuaries subsurface sediments are anaerobic and hydrocarbon oxidation is extremely slow.

After introduction of oil into sediment there is a large increase in the hydrocarbon-degrading microbial population on the surface (ZoBell and Prokop, 1966; Walker et al., 1975). Straight-chain alkanes are rapidly degraded by a mixed community of hydrocarbon-degrading microbes with slower attack on branched-chain alkanes, cycloalkanes and aromatic hydrocarbons (Blumer, 1973; Walker et al., 1973). High-boiling-weight components are very resistant to microbial degradation. Different crude and refined oils show different rates of degradation because of variations in the relative amounts of different oil components. In one experiment, hydrocarbon-degrading microbes were allowed to act on two crude oils (South Louisiana and Kuwait) and two refined oils (Bunker C and No. 2 fuel oil). The South Louisiana crude oil was most susceptible to microbial degradation and the Bunker C oil was the least degraded in the 28-day study (Walker et al., 1976). The high content of high-molecular-weight polycyclic aromatic hydrocarbons in Bunker C oil may explain its resistant to degradation.

In areas with low concentration of hydrocarbons, the hydrocarbon degradation curves show an initial lag with a gradual increase in the rate of degradation (Fig. 11). After the sediments have been exposed to oil for some time the rate of microbial degradation shows a linear curve (Fig. 11). There is no lag period due to a large increase in microbes in the log phase of growth which are able to rapidly degrade many of the oil components.

In addition to microbes, marine sediments contain macrofauna and an interstitial community called the meiofauna, which is composed of harpactoicoid copepods, nematodes, turbellarians and polychaetes (Marc, 1942). Many of these benthic species are deposit feeders that are important in the oxidation and recycling of sediment organic matter (Tenore et al., 1977). In undisturbed sediment most microbial activity is restricted to the surface, but the feeding processes of benthic animals result in sediment turnover to depths as great as 15 m (Rhoads, 1967), thus allowing microbes to degrade organic matter from deeper sediments. Certain polychaete worms, such as *Capitella capitata*, are associated with areas of high oil input (Reish, 1971; Sanders et al., 1972). Cell-free extracts of *C. capitata* and other polychaetes have hydrocarbon-metabolizing enzymes, and living animals take up polycyclic aromatic hydrocarbons from the sediment and metabolize them to various hydroxylated derivatives (Lee et al., 1979). In addition, polychaetes and other benthic animals can enhance microbial degradation of subsurface oil hydrocarbons (Gordon et al., 1978; W. S. Gardner et al., 1979; Lee et al., 1979; Fig. 12.).

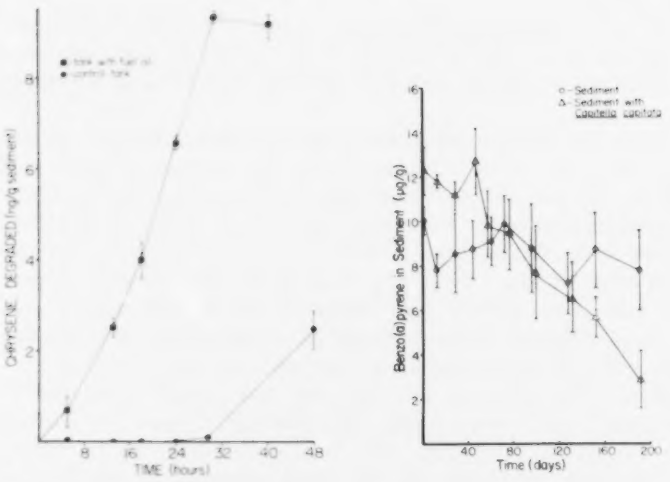

Fig. 11. Amount of ^{14}C-chrysene degraded with time in sediment from fuel oil and control tanks.
One tank containing Narragansett Bay, Rhode Island, water and sediment was continually treated with dispersions of fuel oil over a 3-month period while a second tank served as control. ^{14}C-chrysene (6.3 mCi mM^{-1}) was added to sediment—water slurries from either the control or a fuel oil treated tank to give a concentration of 2.5 μg per gram sediment. Amount of degradation was determined by collecting $^{14}CO_2$ produced at the different time intervals indicated. Temperature was 23° C. A complete description of the procedures used are given in Gearing et al. (1979).

Fig 12. Changes in sediment benzo(a)pyrene concentration with and without the polychaete, *Capitella capitata*.
5 ml of Kuwait crude oil, enriched with 50 mg of benzo(a)pyrene were mixed in trays containing 2000 g of estuarine sediment. Three trays were seeded with *C. capitata* (20 worms per tray) and at various time intervals cores were taken from each tray for the extraction of hydrocarbons. The standard deviation for the benzo(a)pyrene concentration in three trays is shown at each time interval. A complete description of the experiment is given in Lee et al. (1979).

CONCLUSIONS AND SUMMARY

The fate of oil spilled at sea depends on the composition of the oil, and on such external factors as light and temperature. The extent of degradation depends on the type of coastal areas in which the spill occurs. In open, exposed areas, with good circulation of water, most oils are quickly degraded (Rashid, 1974). In protected shallow areas with poor-circulation spilled oil is incorporated into the fine sediment and much remains unaltered for many years (Blumer and Sass, 1972). Photochemical oxidation, dissolution, emulsification, adsorption to particles, biodegradation and uptake by zooplankton

interact to affect the fate of oil slicks and oil in the water. Sedimentation deposits oil on the bottom where it can be resuspended into the water, penetrate deeper into the sediment or be degraded. The sediment community of microbes, meiofauna and macrofauna is responsible for the degradation of sediment oil.

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